Chemical Implications due to the low Electrical Breakdown in the Martian Atmosphere

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Abstract—**This paper addresses the possibility that the chemical reactions observed by the Viking landers on Mars may be a consequence of chemically reactive species on the surface of particles as a result of glow discharge. Triboelectrically charged particles due to the presence of daily dust devils and planetary-encompassing dust storms coupled with the low-pressure atmospheric breakdown in the Martian atmosphere suggests that glow discharge is a prominent characteristic of the Martian environment.**

I. Introduction

The results of the Viking biological experiments on Mars suggest that the soil is chemically reactive [1]. In particular, results of the gas exchange experiment (GEX) show anomalously high concentrations of oxygen released upon humidification of the soil [2]. Even though the findings suggest the presence of biological activity, failure to detect organics using the gas chromatograph mass spectrometer has led researchers to suggest that the reactivity resulted from reduction-oxidation processes in the soil. Although the accepted

hypothesis is the presence of inorganic oxidants on the surface of the soil, there is much debate as to the nature and identification of the oxidant species.

Mineral reactions under the presence of ultraviolet light served as the primary laboratory experiments to reveal inorganic oxidants in the soil. This work was primarily motivated by Huguenin [3] who showed remarkably high oxidation rates for magnetite and basaltic glass under UV irradiation in a simulated Martian atmosphere. However, other researchers were unable to reproduce his results [4,5]. Only in the presence of H_2O were researchers able to reproduce the results of the GEX experiments using UV irradiation to oxidize samples in a simulated Martian environment [6]. The main conclusion is that the reactivity observed experimentally is more likely due to the photochemistry of adsorbed H_2O and its decomposition products, rather than to UV irradiation alone.

Experimental techniques utilizing Electron Paramagnetic Resonance (EPR) identified the superoxide radical O_2^- as the species possibly responsible for the chemically reactive surface. Yen [7] exposed labradorite, a plagioclase feldspar, to UV irradiation in a low humidity environment in simulated Martian conditions. Their results state that the stability, mobility, and reactivity of O_2^- are all consistent with the release of O_2 upon humidification from the Viking experiments through the reaction $2O_2^- + H_2O \rightarrow O_2 + HO_2^- + OH^-$.

Models of the photochemistry of the Martian atmosphere [8-10] suggest that peroxides such as H_2O_2 and superoxides such as HO_2 and KO_2 are the likely oxidants. The reaction with water vapor to produce molecular oxygen makes superoxides particularly attractive. However, they are not believed to be stable on the Martian surface [1] and there are no Martian production methods available to provide bulk superoxides.

Other attempts to reproduce the Viking data were successfully performed by Ballou *et al.*, [11] who used radio frequency (RF) glow discharges in a simulated Martian atmosphere in "an attempt to accelerate the kinds of reactions possible between a soil and the naturally occurring active oxygen species at the surface of Mars." They believe RF glow discharge simulates the formation of reactive species created during long exposure to UV irradiation and that the Viking GEX experiments were a result of oxygen adsorption in strongly bound chemisorbed states or as active oxygen compounds (peroxide, superoxide, or hydroperoxide) that decompose in a humid atmosphere. Oxygen plasma is one of the most powerful oxidants known, thus it is not surprising that it oxidized not only the surfaces of the soil materials but was also able to oxidize H_2O upon exposure.

A method proposed by Mills [12] and again by Oyama [13] suggests that triboelectric charge generated between dust particles during dust storms is capable of creating oxygen plasmas directly on Mars. The high probability for dust interactions during Martian dust storms and dust devils combined with the cold, dry climate of Mars most likely result in airborne dust that is highly charged. Such high electrostatic potentials generated during dust storms on

Earth are not permitted in the low-pressure CO_2 environment on Mars. Therefore electrostatic energy released in the form of glow discharges is a highly likely phenomenon on Mars. Since glow discharge methods are used for cleaning surfaces throughout industry, it was speculated by Mills that dust in the Martian atmosphere undergoes a cleaning action many times over geologic time scales.

Glow discharge on Mars also may induce the dissociation of gases in the atmosphere by the emission of ultraviolet light leading to the formation of gas ions, free radicals, atomic oxygen and ozone. These products are likely to diffuse into subsurface sites in the Martian regolith and provide powerful oxidizing effects that could form peroxides, superoxides and percarbonates. These chemical products likely will interact with the surfaces of soils particles on Mars and may destroy carbonaceous chondritic deposits or other organic materials. Furthermore, microorganisms do not survive for long periods of exposure to glow discharges and their products.

Contact and frictional electrification

There is no unified theory describing the expected magnitude and sign of charge transferred during contact and frictional electrification of insulators. However, the contact charging between metals is well understood. The amount of charge exchanged is related to the contact potential difference and the capacitance between metals. The capacitance is easily calculable through geometrical considerations while the potential is the difference between the metals' work functions divided by the elementary charge. The work function of a metal is defined as the lowest energy required for electrons to be released from the bulk and is usually of the order 4–5 eV. Electrons are transferred between metals until they reach equilibrium.

Electron transfer is also the primary mechanism for metal-insulator contact. Charging depends on the highest occupied energy level (Fermi level) for the metal and the localized energy states available on the surface of the insulator. Several experiments have found that the amount of charge deposited on the insulator varied linearly with the metal work function. Therefore it is customary to define and insulator's work function which was done for the Mars-1 Martian simulant [14].

Sternovsky [15] measured the work function for the Mars and Lunar simulant by contacting particles with several metals and measuring the resulting charge of the particle using a Faraday cup. Materials with a lower work function will charge the simulant negatively and vice versa. There was significant charging of the 125-150 μm particles agitated by the vibrating metal plate. Plotting the charge measured against the known work function for the metals used, a linear extrapolation to zero charge corresponds to the work function of the simulant. Using this method, Sternovsky found the work function for the Mars simulant to be 5.6 eV.

Contact charging between metals and insulators is not limited by the current tunneling process, thus charging densities of the order $\sigma \sim 10^{-5} - 10^{-3}$ C/m^2 are commonly observed [16]. Harper estimated the electric field intensity above a charged spot on a grain to be $E = \sigma/\varepsilon_o(\varepsilon_r+1)$ where E is in the range $10^5 - 10^7$ V/m, ε_0 is the permittivity of free space (8.85×10^{-12} C^2/N·m^2) and ε_r is the dielectric constant of the particle. This field is known to approach the dielectric strength of many insulators. Methods for determining the dielectric properties by remote earth based radar and microwave radiometry have shown that the soil is consistent with that of lunar materials [17] and of dry or frozen terrestrial silicates [18]. The dielectric permittivity was found to be independent of frequency and is given by $k = 1.93^d$ where d is the dry bulk density in g/cm^3. For typical silicate rocks, the density is estimated to be about $2-3$ g/cm^3 resulting in a dielectric constant for the Martian soil ranging between $3.7-7.2$. However, the dielectric properties have never been tested directly on Mars.

Likelihood of dust charging

The primary source for charge buildup on Earth is electrostatic charge generation on ice particles in thunderstorms. However, on Mars the primary source for electrostatic charge generation is believed to be due to contact and frictional electrification during dust devils and dust storms. The high frequency of dust devil activity in some regions and seasons [19] and the presence of local and global dust storms [20] produce a favorable environment for inter-particle contact charging. This charging is exacerbated by the low humidities in the dry Martian atmosphere. The wind mixes the dry dust and could produce bipolarly charged dust clouds as happens for both terrestrial dust devils [21] and volcanic dust plumes [22]. Since grain electrification is easier to obtain in the low-pressure dry atmosphere of Mars [23], there is a good possibility that dust raised during storms would undergo intense electrification.

Particle-particle contacts are also a requirement for many models for dust raising in the atmosphere. Dust can be raised from the surface in many locations [20] and the dominant process known as saltation is believed to be one in which small grains of dust are lifted off the surface due to impact of a dust-laden flow [24]. Other mechanisms include dust devils [25]; the presence of triggering particles [26]; and the clumping of fine grains that produce particles of larger, more easily moved sizes [27]. Most of these models could lead to highly charged particles.

There appears to be other methods for charging dust. Experiments have shown [28] that soil and dust particles acquire a charge due to incident UV radiation. Electrons that are released from the surface of these particles form what is called a photoelectron sheath a few centimeters off the surface.

Even though the dust concentration is estimated to be $\sim$5 particle/cm^3 recent numerical simulations show that the number of particle-particle contacts is more than sufficient to raise the electrostatic potential well above the breakdown limit of the atmosphere on Mars. Melnik and Parrot [29] were able to

numerically model a vortex and wind parallel to a surface encountering a small hill using gravitational, viscous and electrostatic forces only. The assumptions in their model included a charge exchange per radius per particle of 1 fC/μm (10^{-15} C/μm), a reasonable value suggested by Eden and Vonnegut [23]. A preliminary simulation first estimated that the number of particle-particle contacts ranged from 10^4 to 10^7 collisions per cubic meter per second based on number densities of 10^6-10^7 m^{-3} and wind velocities of 30-60 m/s. For the vortex simulation they used a Gaussian particle size distribution centered on 50 μm, a dust particle density of 5×10^6 m^{-3} and an average wind velocity of 40 m/s. The program was set up so that the heavier particles charged positive and the smaller particles charged negative as observed for silica dust clouds by Ette [30] and experimentally by Stow [31]. Melnik and Parrot [29] showed that within a few seconds (~6 seconds) the electrical field strength at breakdown of 20 kV m^{-1} was achieved. Even after significantly reducing the number density (2 cm^{-3}) while keeping the grain charge (1 fC/μm) and using a higher density (5 cm^{-3}) with a reduced grain charge (0.5 fC/μm) were they able to increase the time before breakdown to 72 seconds and 97 seconds respectively.

The second simulation assumed a wind velocity of 40 m/s encountering a hill with a slope of 11°. The growth of the charge is exponential and breakdown is reached very quickly in about 13 seconds. The particle density at the top of the hill was 5 cm^{-3} where breakdown occurred. Using conservative estimates for particle concentration, charge exchanged during contact, and wind speeds, both models clearly show that electrical breakdown due to triboelectricity may occur frequently. However it should be noted that all of the above assume a Martian atmosphere composed of 100% CO_2 and that one must be cautioned that breakdown (or Paschen) measurements are highly dependent on gas composition and even a very small amount (<0.1%) of mixing gases radically changes the curve, as noted by Leach [32] (see figure 1 below). Therefore, we present Paschen measurements using a Mars gas mixture.
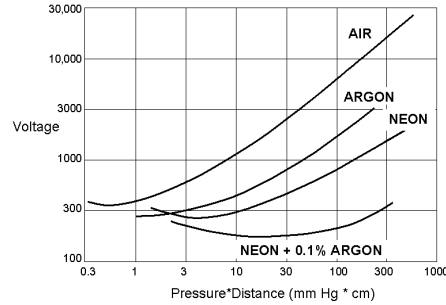

Fig. 1. Paschen measurements with minimal changes in atmospheric gas content [32].

II. PASCHEN MEASUREMENTS OF A MARS GAS MIXTURE

Gas discharge phenomena can generally be divided into those that occur at low pressure ($\leq$ 100 torr) such as glow discharge, and those that occur at high pressures ($\geq$ 760 torr) such as corona or spark discharges. Arc discharges can occur under both high and low pressures. Glow discharges typically have high electron temperatures (1-5 eV) and low gas temperatures (300K − 500K). The generated electrons tend to cause a relatively low degree of ionization (~10^{-6}) in the gas, and the charge particle density is of the order 10^6–10^{13} cm^{-3}.

In a first attempt to understand the electrostatic charging of particles on Mars, Paschen measurements are taken using a Mars gas mixture that relate the minimum potential required to spark across a gap between two electrodes. The minimum potential is plotted versus the pressure-distance value for electrodes of a given geometry. For most gases, the potential decreases as the pressure decreases. For CO_2, the minimum in the curve happens to be at Mars atmospheric pressures (5-7 mm Hg) for many distances and geometries. Here, we present the experimental results of a Paschen curve for a Mars gas mixture compared with 100% pure CO_2.

Procedure: The experiments were performed using voltages of either positive or negative polarity applied to one custom-made brass electrode while the other was grounded. The cylindrical electrodes had a diameter of 5.059 cm (2 in.) with curved edges to eliminate edge effects that create strong electric fields and they were fixed at 0.1 cm apart providing parallel-plate geometry.

The chamber was pumped down to 10^{-4} mm Hg and backfilled to ~ 50 mm Hg with the atmospheric gas. It was pumped down again to remove residual gases and contaminants. The gases that were used are 100% CO_2 and a Mars gas mixture provided by Praxair Inc. that consisted of 95.5% carbon dioxide, 2.7% nitrogen, 1.6% argon, 0.13% oxygen, and 0.07% carbon monoxide.
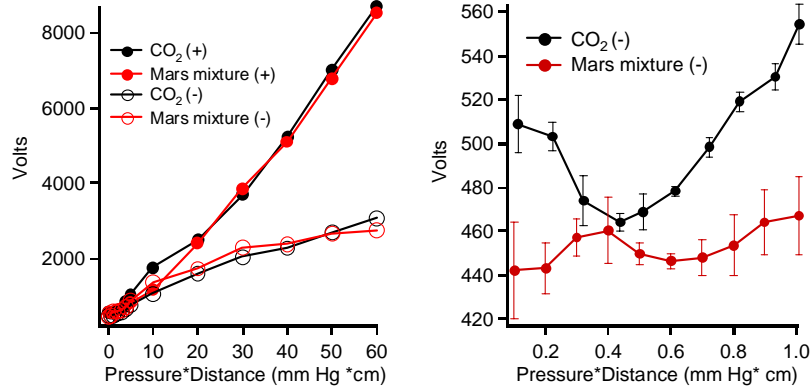

Fig. 2. Paschen measurements for a Mars gas mixture compared with CO_2. (The error bars are smaller than the points.)

Results: Measurements were taken by simply increasing the voltage until the power supply shuts off as a result of the current divergence during breakdown. Figure 2 shows the minimum voltage required for electrical breakdown of the two gases for both positive and negative polarities. Clearly, as the pressure is lowered, less voltage is required for breakdown to occur for both gases. At the higher pressures the spark potential does not seem to depend on the makeup of the gases but depends strongly on the polarity of the voltage applied. This is mainly due to the fact the negative potential electrode releases electrons from the metal that ionizes the CO_2 molecules easily. These ionized molecules increase in number very rapidly and eventually form a current path to ground. However, a positive electrode does not release electrons and breakdown must occur using the more massive and slower positive ions in the gas. An excellent review of Paschen breakdown is given in [33] and in Cobine [34].

However, at lower pressures, a clear difference in breakdown potentials can be seen. Figure 2 shows how the small concentrations of nitrogen, oxygen, argon, and carbon monoxide greatly alter the Paschen curve for pressures ranging between 1 and 10 mm Hg. We can see that the minimum in the CO_2 curve at around 4-5 mm Hg becomes shifted to 6-7 mm Hg once the other gases are added. This suggests that even though breakdown occurs easily at Mars pressures (~ 20–25 kV/m), it may not occur at the minimum in the Paschen curve for CO_2. Instead the results seem to indicate that there may actually be a local maximum near the minimum in the CO_2 curve.

Verification of glow discharge by triboelectric charging

So far we have shown that the dust is most likely charged and that the atmosphere supports a significantly lower potential for electrical breakdown. Although there is no evidence for electrostatic breakdown in the form of glow discharge on Mars, there are a few laboratory experiments that support the possibility.

Eden and Vonnegut [23] showed that dust motion might be a source of charge generation in the Martian atmosphere. They performed an experiment in which a 1-liter glass flask containing 50 g of dried sand in an atmosphere of CO_2 evacuated to 10 mm-Hg. The flask electrodes were placed outside 10 cm apart and the flask was shaken vigorously. They observed several modes of electrical breakdown including (1) small sparks, (2) bright discharges several centimeters long and one centimeter wide, and (3) a faint extensive glow discharge. The dominant colors were from the blue to red parts of the spectrum and the minimum intensity was of the order 10^{-4} mlam.

Dust movement was not necessary to produce similar discharges when 1200 volts were applied to the electrodes. After agitation, voltages up to 500 V were induced between the electrodes and the inside surface of the flask became highly coated with particles which adhered strongly. They also estimated about 10^4 elementary charges per particle or 1.6 fC (1.6×10^{-15} C) [35].

Mills [12] performed a similar experiment in which a 5-liter flask was rotated manually to agitate dust. Again using dried sand and air as the gaseous medium, several discharges were observed. At 0.1 torr a faint greenish-white glow extended for more than 5 cm above the surface. Between 4-6 torr, the glow contracted and brightened and was accompanied by long, forked, ribbon discharges about 1 cm wide. He noted a 'twinkling' appearance as the discharges darted through the dispersed, moving sand. At 10 torr the ribbon discharges became brighter but less frequent until 50 torr was reached, where bright twinkle discharges remained.

Preliminary tests were performed by Oyama and Berdahl [13] in which rock-fragments were tumbled in a wide range of pressures for individual constituents of the Martian atmosphere (CO_2, CO, O_2, N_2 and Ar). Electron energies of 450 eV were sufficient to produce excited CO* which is required for C_3O_2 formation. They believed that the active species in the plasma cause the formation of carbon suboxide, which is immediately adsorbed on surfaces or reacts with already adsorbed C_3O_2 monomers. The adsorption of these monomers and polymers on surfaces is believed to explain the results of the Viking experiments.

We recently redid this experiment [36] but instead of using dry sand, we used dry Mars-1 Martian soil simulant [14] immersed in a Mars gas mixture provided by Praxair Inc. (see section II). The simulant was placed inside an Erlenmeyer flask and evacuated below 10 mtorr. It was then backfilled with the Mars gas mixture and capped off and removed from the vacuum. After a few minutes in the darkroom, the flask was shaken vigorously and several discharges were observed. Approximately 90% of the discharges were green sparks while the rest were bluish purple. Red spark discharges were not observed in contrast to Eden and Vonnegut. All of the above experiments, along with what is known about the Martian environment, suggest that glow discharge is a likely phenomenon on Mars.

Implications for Mars

There are perhaps profound consequences for glow discharges on Mars. The primary ions resulting from electron-molecule collisions in air are N_2^+ and O_2^+ positive ions and O_2^- and O^- negative ions. But these primary ions react rapidly with H_2O and CO_2 to form more complex ions, mainly $H_3O^+(H_2O)_n$ with some $NH_4^+(H_2O)_n$ positive ions and in hydrated form NO_2^-, NO_3^-, CO_3^-, and CO_4^- negative ions [37].

However, most of the energy (about 99%) is transferred to the neutral gas. Although some energy will be transferred in the form of heat, the remaining will participate in activation reactions through electron-molecule nonionizing collisions (~1-10 eV) resulting in high production rates of dissociated molecules, radicals (N, O, OH, …) and excited species (N_2^*, N^*, O_2^*, O^*). Reactions between all of these species lead to the formation of new chemically active

products such as O_3, H_2O_2, NO_x, HNO_2 and HNO_3 molecules [38]. Ultraviolet radiation is also a consequence of glow discharge.

The primary effect of glow discharge on surfaces is chemical modifications of the surface layer composed of the degradation products loosely bound to the surface [39]. These degradation products are highly oxidizing functions capable of transforming the surface properties by increasing wettability (hydrophilicity [40]), adhesivity, and porosity [41] as well as new electrical properties [42]. Hence, glow discharges are commonly used throughout industry to transform the surface properties of polymers systematically in a known way.

Powerful techniques such as X-ray photoelectron spectroscopy (XPS) are used to identify the chemical changes on the surface. Experiments [43] show that polyethylene, normally hydrophobic, becomes wettable upon exposure to oxygen plasmas. XPS data shows decreasing carbon peaks with a corresponding increase of oxygen peaks, which indicate the formation of functional groups such as carboxyl and hydroxyl groups on the surface.

Similar measurements on low-density polyethylene (LDPE) performed by Dai *et al.*, [44] show surface energy increases upon exposure to glow discharge. They identified the following carbon groups using XPS: saturated carbon at 285.0 eV, carbon bonded to one oxygen at 286.1 eV, carbon singly bonded to two oxygen atoms or double bonded to one oxygen atom at 287.6 eV, and carbon singly bonded to three oxygen atoms or carboxyl groups at 289.3 eV.

The polarity of the discharge also affects the chemical nature of the surface. Experiments by Jouve *et al.*, [45] using glow discharge on moist metal surfaces have shown using XPS that *oxidation* occurs using a negative polarity while *reduction* occurs when exposed to positive glow discharge. They stipulate that gas/surface interactions proceed through an interface chemistry in the liquid phase. The importance of the presence of moisture indicates the acid nature of the gas/surface interface.

The general consensus is that highly reactive neutral products, combined with the presence of water in glow discharges are responsible for the chemical changes on the surface. This is supported by Goosens *et al.*, [46] who used Electron Spin Resonance (ESR) to identify free radicals that are long lived in plasma polymers from ethylene, propylene, and ethylene oxide. ESR confirmed the presence of free radicals in ethylene and propylene; however, ethylene oxide did not reveal any detectable signal from remaining radicals. They suggested that the case for ethylene and propylene the presence of remaining double bonds is expected to have a stabilizing effect on some radical sites since radicals become less reactive by delocalizing across several atoms.

Even though we concede that UV irradiation on the surface of Mars accounts for a majority of the oxidants present (in what is still an unknown process), we believe that glow discharge as a result of triboelectrically charged particles above the breakdown limit in the Martian atmosphere may be a more *efficient* process creating oxidants on the surface. This stems not only from the

ability of glow discharges to provide a direct source of free radicals but from the results of biological experiments that prove that UV from glow discharge is in some ways more efficient for sterilization than UV from lamps.

Sterilization of bacteria

Recent work involved in the sterilization of medical products through the use of glow discharge has been performed by several researchers [47-49]. These techniques are highly desirable since the conventional method used to sterilize medical instruments involves toxic gases such as ethylene oxide and its mixtures with chlorofluorocarbons, which commonly pose a health risk and are environmentally unfriendly.

Soloshenko *et al.*, [47] created a plasma using DC glow discharges in a variety of gases under pressures between 0.02 to 0.25 torr. The electron energy distribution functions (EEDF) were measured using standard Langmuir probes. The measured plasma density (7×10^8 to 6×10^9 cm^{-3}) varied linearly with increasing input power (3×10^{-3} to 30×10^{-3} W/cm^3) and the electric field varied from 0.1 V/cm to about 1.0 V/cm. The UV radiation intensity increased with increasing the input power density (3-7×10^{-3} W/cm^3) and the bulk of the UV power (50-100 $\mu W/cm^2$) was emitted from the plasma at wavelengths $\lambda \leq 220$ nm.

These biological investigations were carried out using *Bacillus subtilis*, common bacterium known to be resistive to glow discharge plasmas. The number of spores on the Petri dishes varied between 10^5 to 10^8. After exposed to the glow discharge, the spores were incubated and the number of spores that survived the sterilization were plotted (Kill curves). The research focused on identifying which of the three primary effects of glow discharge are responsible for sterilization. These are: (1) the effects of charged plasma particles, (2) the effects of ultraviolet radiation and, (3) the effects of chemically active neutral plasma particles such as free radicals and excited atoms or molecules.

By varying the potential on the metal test subjects, these researchers were able to change the electron and ion fluxes onto the bacterium. If charged plasma particles play a major role in sterilization processes, then this process should be a function of the applied potential. Test subjects held at the anode, cathode, or floating potentials exhibited survivability times nearly identical indicating that charged plasma particles were not responsible for sterilization.
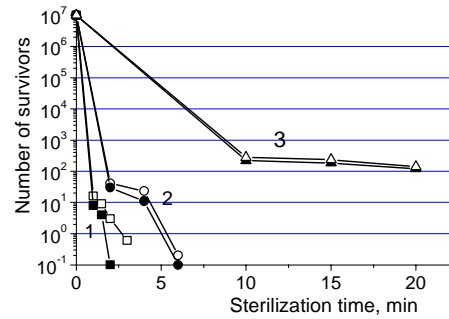
Fig. 3. Survival curves for spores *B. subtilis*. P=0.2 Torr, W_d=0.003 W/cm^2. 1 – oxygen, 2 – air, 3 – nitrogen. Open symbols – tests under UV filter KU-1, solid symbols – tests open. Initial population – 10^7 spores *B. subtilis.* Circles – 0.08 Torr, squares – 0.2 Torr.

To study the effects of UV on the samples, experiments were performed to sterilize the samples either directly or through filters made of lithium fluoride (LiF) (allow wavelengths $\lambda \geq 120$ nm) and KU-1 quartz glass ($\lambda \geq 160$ nm). Figure 3 shows the combined action of reactive neutral particles and UV radiation and exclusively by UV radiation in discharge plasmas for O_2, air and N_2.

These experiments show that the main role in sterilization by glow discharge in dry gases is played by UV radiation and that the most efficient working gas was oxygen followed by air, CO_2, H_2, Ar, and N_2 in decreasing order [47]. Clearly, UV irradiation plays the major role in sterilization and similar results were found using LiF filters over the entire range of pressure and specific input power for all working gases studied. Also, a photoresist showed that the longest wavelength emitted from the discharge was ~220 nm. This suggests that sterilization by UV radiation with wavelengths in the range $160 \leq \lambda \leq 220$ nm is the most efficient. These experiments point out that sterilization efficiency is significantly higher than conventional UV radiation from mercury lamps which output much longer wavelengths ~253 nm.

For determining the relative contribution of chemically reactive neutral plasma products, these researchers used a small mesh grid for reflection of the charged plasma as well as a shield opaque to UV radiation, which was installed behind the grid for reflection, and absorption of UV radiation. Thus, test objects placed behind the grid and shield could be only reached by non-charged active plasma particles. The results indicate that although these reactive particles participate in the sterilization process, UV still plays the dominant role for dry gases. However, materials with complicated shapes (such as Mars regolith for example) are not sterilized by incident UV radiation due to shadowing effects, thus chemically reactive neutral species may become the dominant mechanism for sterilization.
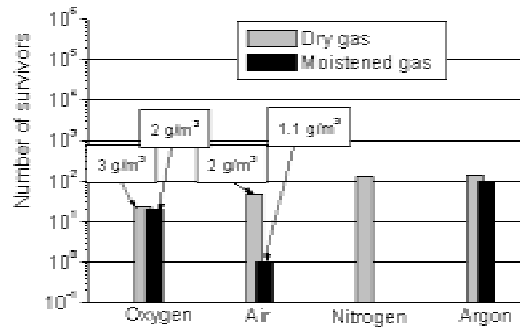
Fig. 4. Comparison of sterilizing ability of discharge in various dry (45% RH) and moistened (90% RH) gases. Ozone concentration is shown for oxygen and air.

The results of these experiments go on further to show the role of moisture on the survival rates of bacteria under glow discharges. Figure 4 shows results for dry and moistened oxygen, air, nitrogen, and argon. For dry gases the most efficient sterilization is in oxygen (due to the highest ozone shown in boxes) followed by air, nitrogen and argon as before. Oxygen moistening results in a decrease of ozone concentration, with the efficiency of the sterilization process remaining unchanged. At the same time, moistening the air results in increased sterilization accompanied by a decrease in ozone concentration.

Furthermore, in addition to ozone, experiments show by using numerical models of the plasma concentration that other chemically reactive species present (such as hydrogen peroxide nitrogen oxides, nitric and nitrous acids) may all be responsible for the sterilization [49]. This model shows that the observed increase of the sterilization efficiency under air moistening is due to biologically active particles such as hydrogen peroxide H_2O_2, nitric HNO_3, and nitrous HNO_2 acids, HO_2NO_2 radicals and the growth of N_2O and N_2O_5 concentrations.

Thus the main conclusions of these works are: (1) UV emitted by the glow discharge plays the dominant role in sterilization with wavelengths 160 to about 220 nm; (2) items with complicated shapes are more easily sterilized through chemically reactive species in the discharge; and (3) the significant sterilization efficiency occurring in air in the presence of moisture results from the production of hydrogen peroxide, nitric and nitrous acids, free radicals and other biologically active particles.

III. CONCLUSIONS

The Mars solar constant based on the solar spectrum [50-52] show that the UV irradiation incident on Mars starts above 200 nm due to the strong absorption by CO_2 around 190 nm. Thus UV below 200 nm is not expected to reach the surface of Mars. Therefore, we believe that although the majority of the

oxidation is due to the solar UV irradiation and its influence on the photochemistry of H_2O on surfaces, we also suggest that glow discharge resulting from highly charged particles is a more efficient process for oxidation. This is based on the following conclusions: (1) the low pressure atmosphere combined with the daily occurrences of dust devil makes tribocharging followed by glow discharge a very likely phenomenon on Mars working both day or night; (2) materials immersed in glow discharge are subjected directly to chemically reactive species which are known to oxidize surfaces; and (3) the wavelength of the UV radiation emitted from glow discharges is known to be much more effective for killing bacteria than the wavelengths of solar incident UV irradiation.

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